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(54) TREATMENT FOR SURFACE OF METALLIC MATERIAL

(57) Abstract:

PURPOSE: To inexpensively form a rigid coated layer with a sufficient thickness free from defects such as dimensional changes, deterioration in the hardness (strength) of a base metal and film peeling caused by holding the temp. of the whole body of the metallic materials of a base metal to a high one.

CONSTITUTION: The surface of a base metal constituted of metallic materials is coated with metallic or nonmetallic materials. After that, the deposits are remelted for each minute area by pulse electric discharge machining in liq., gas or vacuum, by which the base metal and the coated materials, are diffused and mixed to form a dense coated layer on the surface of the base metal. As the coating materials, metals, alloys, nonmetallic elements, ceramics, carbides, nitrides, borides or the like are used. As the coating means for the coating materials, a thermal spraying method, an electrodepositing method, a low temp. depositing method, a discharge precipitating method using an electrode easy to consume or the like are used. As for the pulse electric discharge machining, it is executed preferably by using an electrode hard to consume as a minus electrode. The material called as a functionally gradient material in which the coating of the coating materials and pulse electric discharge machining are executed per layer and the coated layer is provided with gradient properties can also be manufactured.

CLAIMS

[Claim(s)]
[Claim 1] The surface treatment method of the metallic material characterized by diffusing this covering material, mixing with a base material, and forming a precise enveloping layer in a base material front face by making this sediment remelt for every minute field by the pulse electron discharge method in liquid, a gas, or a vacuum after covering a metal or a nonmetal material on the base material front face which consists of a metallic material.
[Claim 2] The way according to claim 1 covering material consists of one sort of a metal or an alloy, a nonmetallic element, ceramics, carbide, a nitride, and a boride, or two sorts or more.
[Claim 3] The way according to claim 1 the covering means of covering material is a spraying process, an electrodeposition process, a lowtemperature-evaporation method, or the electric discharge depositing method using the electrode which is easy to exhaust.
[Claim 4] A pulse electron discharge method is a method according to claim 1 of performing the electrode which is hard to exhaust as a minus pole.
[Claim 5] The method according to claim 1 of performing covering and the pulse electron discharge method of covering material for every layer, and giving lopsidedness to an enveloping layer.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001] this invention is started and based on the surface treatment technology of a metallic material, in detail, has neither the dimensional change of a base material, nor the problem of the heat history, and relates to the surface treatment method which forms in a front face the precise layer which has desired properties, such as thermal resistance, corrosion resistance, abrasion resistance, and a degree of hardness
[0002]
[Description of the Prior Art] Conventionally, CVD (chemical vacuum deposition), PVD (vacuum deposition), electrodeposition, nitriding, electrochemical plating, electroless plating, etc. are known as a means for giving abrasion resistance, corrosion resistance, etc. to a surface of metal.
[0003] However, in order that each of CVD(s) and PVD(s) may go up and coat the temperature of a base material to 360 degrees C or more and about 1100 degrees C, it is known widely that there is a fault that a base material produces a dimensional change or a degree of hardness fall. A hardening layer is also as thin as several micrometers. Moreover, nitriding also has the difficulty of heating and processing steel materials at about 500 degrees C.
[0004] Since a deposit metal only accumulates or deposits in a base material and the front face by electrodeposition is not diffused, it is known well that it will be easy to exfoliate, and there is a fault, such as producing hydrogen embrittlement. The same is said of the case of electrochemical plating and electroless plating.
[0005] It is already known that the thing made to deposit on a base material front face by thermal spraying will be porosity, and it will be easy to exfoliate. Moreover, since heat input becomes uneven with the position of a spot and a striation is generated on the boundary of beam advance even if you are going to make it remelt this by the laser beam, a beautiful front face cannot be obtained. Moreover, in a laser beam, application is difficult for the processing configuration of three dimensions as shown in drawing 1on structure.
[0006] Moreover, it is difficult to coat with the conventional surface treatment method the material which is [fine ceramics] hard to diffuse by sufficient thickness (an example, several 10 micrometers - 100 micrometers), since diffusion hardly arises.
[0007] this invention solves the trouble of the abovementioned conventional technology, does not have faults, such as a fall of the degree of hardness (intensity) of the dimensional change produced by maintaining the whole metallic material of a base material at an elevated temperature, and a base material, and coat ablation, and aims at offering the surface treatment method which can form the firm enveloping layer which moreover has the surface characteristics of a request of **, such as corrosion resistance and thermal resistance, by sufficient thickness.
[0008]
[Means for Solving the Problem] In order to solve the aforementioned technical problem, this invention persons repeated research wholeheartedly first about the surface treatment method which does not have the **** need in an elevated temperature in the whole metallic material.
Consequently, covering material was deposited by the method of not heating temperature of a base material to an elevated temperature on the surface of a metallic material, if it remelted in the minute field, and it could be spread in the base material and it could be made to mix the sediment microscopically, neither deformation of a base material nor a degree of hardness fall was generated,

but knowledge that a firm enveloping layer can moreover be formed was acquired.
[0009] Then, whenresearch was further repeated about such a policy that may remelt a sediment microscopically, the possible thing was found out by applying a pulse electron discharge method. Although the electron discharge method was the processing method generally well learned as a processing method which carries out removal processing of the configuration using an electric discharge phenomenon, this invention persons developed the completely new directions of remelting a sediment microscopically by the energy of electric discharge.
[0010] That is, after this invention covers a metal or a nonmetal material on the base material front face which consists of a metallic material, by making this sediment remelt for every minute field by the pulse electron discharge method in liquid, a gas, or a vacuum, it diffuses this covering material, is mixed with a base material, and makes a summary the surface treatment method of the metallic material characterized by forming a precise enveloping layer in a base material front face.
[0011] this invention is explained still in detail below.
[0012]
[Function]
[0013] As mentioned above, making covering material deposit [adhere it and] and deposit on the front face of a metallic material by thermal spraying, electrodeposition, vacuum evaporationo, and electric discharge deposit is known. In addition, the electric discharge depositing method is a method of depositing green-compact material to the other party metal, when a conductive material which is the surface treatment method proposed previously (the "Japan Society for precision Engineering spring convention academic lecture meeting lecture collected works in the 1991 fiscal year" (March 26, 1991) p.463), and should deposit is fabricated as a green compact, and this invention persons use as an electrode of an electron discharge method and process it. However, since these sediments are not diffused in a base material, its bond strength is weak.
[0014] without it therefore raises most average temperature of a base material for this invention to add pulse electric discharge in liquid, a gas, or a vacuum by the technique of an electron discharge method to such a sediment-- being partial (discharging point) --by generating of high temperature, it remelts and a base material is diffused
[0015] In this invention, as a means to cover covering material on the surface of a metallic material, although there is especially no limit, the method which is not in high temperature **** about a base material is recommended. For example, although the above-mentioned spraying process, an electrodeposition process, a low-temperature-evaporation method, the electric discharge depositing method using the electrode which is easy to exhaust, etc. are mentioned, it is not necessary to say not being restricted to these. If it carries out from a relation with the pulse electron discharge method performed as a back process, the electric discharge depositing method is desirable.
[0016] As covering material, various metallic materials or nonmetal materials are possible, for example, they are a metal or an alloy, a nonmetallic element, ceramics, carbide, a nitride, a boride, etc. concrete-- as hard material-- nitrides (fine ceramics), such as borides, such as carbide, such as WC, TiC, TaC, ZrC, and SiC, and TiB2, ZrB2, and TiN, ZrN, etca simple substance -- or where a sintering acid is added, it can cover Moreover, corrosion resisting materials, such as metallic materials, such as W and Mo, and aluminum, Ti, nickel, Cr, Co, can also be used. Furthermore, even if there is no conductivity like a diamond, aluminum 2O3, and Si3N4, it may mix with conductive material, such as iron powder, cobalt powder, nickel powder, chromium powder, and copper powder, and you may cover. What is necessary is in short, just to choose material due to the surface characteristic made to give.
[0017] After covering covering material on the surface of a metallic material, a pulse electron discharge method is microscopically applied for every minute field, a sediment is remelted, it is spread in a base material and it is mixed. This pulse electron discharge method can carry either in liquid, a gas, and a vacuum out, uses a sediment as one electrode, and generates electric discharge between the electrodes of another side.
[0018] It is desirable to use the electrode which is hard to exhaust on the occasion of a pulse electron discharge method, and to use the electrode of composition near a sediment. For example, when WC is made to deposit on a metallic-material front face as a subject, the material (an example, a byte's chip material) which sintered WC-Co is used for an electrode.

[0019] Electric discharge makes it generate by about 10,000 numbers from hundreds of times in 1 second. A processing side is a front face which small microscopic electric discharge marks accumulated. Although electric discharge marks current density is a minute area, it is as high as tens of thousands A/cm2, and produces elevated temperature high pressure in a short time for several 10 microseconds - about 1000 microseconds. Although the skin temperature of a discharging point turns into a boiling point grade of the material, the pressure of the point serves as several 1000 kgf/cm2 and the dissolved part has some dispersing, the portion which remained is remelted and is diffused in a base material. Since a charging time value is a short time, a discharging point is cooled immediately and the average temperature of a base material does not rise.
[0020] The desirable conditions of a pulse electron discharge method are supply voltage:60000V, pulse discharge current value (Ip):1100A, pulse width (taup):52000microsecond, and quiescent-time (taur):5-2000microsecond. Generally, like [in Ip=50A] taup=2000taus, when the pulse discharge current value Ip is small (for example, when taup=16microsecond and Ip are large in Ip=3A), when Ip is small, taup also takes long taup, when short **** and Ip are large.
[0021] According to the surface treatment method of this invention, the precise layer which has desired properties, such as thermal resistance, corrosion resistance, abrasion resistance, and a degree of hardness, can be formed in the front face of metallic materials, such as ferrous materials, such as cheap carbon steel. Even if it is the material which is hard to diffuse in steel materials like fine ceramics, the diffusion and adhesion to a base material can be strengthened by remelting. Moreover, if the pulse electrodischarge treatment also of the material which is easy to dissolve to a ferrous material like aluminum, Ti, nickel, Cr, and Co is carried out, the still still firmer surface treatment of it will become possible. That is, even if it is the material which is easy to dissolve to a ferrous material like aluminum, Ti, nickel, Cr, and Co, the diffusion to a base material is inadequate, and in order to make speed of an electric discharge deposit quick, when using a high current and performing a high-speed electric discharge deposit, although irregularity becomes intense also in a deposit state, according to the pulse electrodischarge treatment, diffusion by remelting is promoted. Moreover, if plating speed is raised by high current density with electrodeposition or electroplating, although only the rude small plating layer of the adhesion force will be obtained, if a pulse electron discharge method is performed, the large surface layer of the adhesion force can be formed. If a pulse electrodischarge treatment is performed to what mixed and coated the hard material of non conducting, such as a diamond, aluminum 2O3, and Si3N4, with conductive metals, such as iron powder, cobalt powder, nickel powder, chromium powder, and copper powder, a conductive metal will remelt and non-conducting hard material will fix on a base material front face firmly.
[0022] Moreover, material with lopsidedness can also be manufactured. Lopsidedness material is the material which a base material is made into a metallic material, and the content rate of fine ceramics increases gradually from a base material side, and raised the content rate of fine ceramics for the material-list side remarkably. Since it has little generating of the shearing stress of a plane of composition and generating of bending stress by the difference with a remarkable expansion coefficient compared with the material which only joined or coated a metallic material and fine ceramics even if such a lopsidedness material has a temperature rise, fracture in use etc. cannot produce it easily due to high temperature. This is because it is eased as stress, even if the thermal expansion by the temperature rise occurs.
[0023] Next, the example of this invention is shown.
[0024]
[Example 1] The Fe-aluminum alloy layer was obtained on the surface of the base material (S50C, temper material) by electric discharge deposit in the way which compresses the powder of aluminum and is shown in drawing 1 as one electrode. aluminum green compact was used because it would be easy to deposit by electric discharge on a parent metal since apparent thermal conductivity falls in 1 / 2 - 1/3 and the intensity of an electrode material also becomes weak, if it uses by making aluminum into fine particles. It is [Table 1] about electron discharge method conditions.

項　目	Al圧粉体による放電析出加工条件
電極	Al圧粉体、成形圧力：4ton、その他：表3参照
被加工材	S50C(調質材)
加工液	ダイヤモンドEDF
電極極性	(−)
加工条件	Ip：10A、τp：256μs、τr：256μs
加工時間	5min

It is alike and is shown.

[0025] The analysis result according the analysis result by EPMA of the obtained alloy layer to an X diffraction is shown indrawing 2 at drawing 3. Fromdrawing 2, while aluminum of an electrode material has lopsidedness (mostly few [inside] on a front face), it exists in the processing side by 30 micrometers in thickness. Moreover, the peak of very strong AlFe 3C0.5 is seen fromdrawing 3. This compound is known as an intermetallic compound excellent in oxidation resistance. Thus, sufficient surface treatment may be possible for the case of aluminum by electric discharge deposit.

[0026] However, it is difficult for the material of a highmelting point like fine ceramics (WC, TiC, TaC, ZrC, SiC, TiB2, ZrB2, TiN, ZrN, etc.), and W and Mo for you to make it fully spread to the interior of a base material only in an electric discharge deposit in many cases. Then, by this example, the electric discharge deposit of the WC of them is carried out, and the case where pulse electron discharge method processing is applied to this is shown.

[0027] First, it pressed by having mixed WC powder (3 micrometers of mean particle diameters) with Fe powder (9.8 micrometers of mean particle diameters) at a rate of 1:1 (compressionpressure 4 t/cm2), and considered as the green compact. This was pasted up on the copper round bar in the electroconductive glue, and it considered as the electrode. Subsequently, carbon steel (S55C green wood) was used as the base material, processing conditions (Ip, taup, taur) were changed, and the electron discharge method experiment was conducted in the way shown indrawing 1.

[0028] Consequently, although the arc according [D.F (duty factor)] to electric discharge concentrated and the electrode was destroyed on comparatively large processing conditions, on 1.5% or less of conditions, it was stabilized, and D.F was exhausted, without WC electrode collapsing, and adhered to the base material front face. The processing conditions at that time are Ip=20A, taup=16microsecond, and taur=1024microsecond.

[0029] As a result of performing an X diffraction on the sample front face after processing, as shown in drawing 4, the peak of WC appeared. It is [Table 2] as a result of measuring the coating weight (height from a base material front face) of WC by floor to floor time by the depth of focus method.

加工時間 / 加工高さ	20分	30分	50分	90分
中心部(μm)	6.6	11.1	19.6	51.9
縁　部(μm)	5.5	27.1	80.7	65.4

It is alike, and the coating weight of WC on the front face of a base material increases by lengthening floor to floor time so that it may be shown. WC adhering to the base material front face was a thing of a grade which will exfoliate if adhesion force is weak and rubs with a driver etc.

[0030] Next, the pulse electron discharge method was carried out in the following ways into the material obtained by the aforementioned electron discharge method.

[0031] First, the WCCo sintered compact was pasted up on the copper round bar in the electroconductive glue, and it considered as the electrode (finishing electrode). Subsequently, the upper shell pulse electron discharge method of WC and Fe deposit adhering to the base material front face was performed using this finishing electrode. Processing conditions considered electrode

polarity as minus, changed Ip, taup, and taur, and were processed by the circuitry shown in drawing 5 so that a base material might not be processed too much. Pulse shape (square wave) is shown in drawing 6 . The result which carried out the X diffraction of the front face is shown in drawing 7 after processing, and it is [Table 3] about the analysis result.

Ip / τp(τr)	20	10	3
16(1024)	×	○	○
64(256)	○	○	○
1024(1024)	○	○	○

(注) ×：WCは検出されない
○：WCが検出された

It is alike and is shown. As shown in this **, although the sediment ****(ed) when pulse width (taup) was short, current value (Ip) was high and floor to floor time was long, taup was a little long, current value (Ip) could lessen scattering of the sediment of WC-Fe on low conditions a little, and WC was detected.

[0032] In the electric discharge deposit, although the adhesion force of WC-Fe was weak as shown in drawing 8 (cross-section microphotography), when the pulse electron discharge method was performed to this, it was checked that WC is spread in the base material as shown in drawing 9 (cross-section microphotography) and drawing 10(cross-section SEM photograph).

[0033] Moreover, a cross section shows the relation between the distance from a front face, and Vickers hardness number (Hc) todrawing 11 . The degree of hardness of the usual WC-Co alloy is about 800 to 1400 Hv, and the degree of hardness (Hv 1000-1400) (the hardening penetration of S55C is 800 or so Hv(s)) of a surface treatment layer of the same grade as it was accepted in this experiment. Moreover, the thickness which can obtain 1000 or more Hv(s) in this experiment has large thickness at about 60 micrometers.

[0034]

[Example 2] The base material was used as steel materials (special tool steel), and the fine-particles electrode which mixed TiB2 as fine ceramics and mixed Fe powder as an assistant was used. First, the laminating was carried out by the electric discharge deposit by the fine-particles electrode like drawing 12 . Pulse ****** was performed after the laminating. It carried out by being two kinds, the case where a laminating and a pulse electron discharge method are performed for every layer, and after all ending a laminating, when pulse ****** being performed, at that time.

[0035] Consequently, lopsidedness material with the enveloping layer to which the content of TiB2 decreases gradually from a front face was obtained. Moreover, adhesion force etc. was tough although time and effort required former one. In addition, the Vickers hardness number of a part with the Vickers hardness number of the surface section near Hv=2000-2500 and a base material was Hv=550-600.

[0036]

[Example 3] The base material was used as steel materials (special tool steel), and the fine-particles electrode which mixed diamond powder and cobalt powder as hard material was used. First, the laminating was carried out by the electric discharge deposit by the fine-particles electrode like drawing 13 . The pulse electron discharge method was performed after the laminating. It carried out by being two kinds, the case where a laminating and a pulse electron discharge method are performed for every layer, and after all ending a laminating, when pulse ****** being performed, at that time.

[0037] Consequently, lopsidedness material with the enveloping layer to which the content of a diamond decreases gradually from a front face was obtained. In addition, the Vickers hardness number of a part with the Vickers hardness number of the surface section (part with many diamonds) near Hv=3500-4000 and a base material was Hv=550-600.

[0038]

[Example 4] Processing as shown in drawing 1 was performed, and the precise enveloping layer was formed in the inside of a mold by fine ceramics or WC-Co. First, as shown in drawing 1 , three-dimensions configuration processing was performed to the electrode using the material used for the electron discharge methods [exhausting / usual low], such as copper or graphite. Then, thermal spraying which mixed cobalt powder about 20% at TiB2 powder was carried out to the inside of a work. The thickness is about 100 micrometers. The thermal spraying film is deposited a little irregularly, as shown in drawing 14 .

[0039] and pulse electron discharge method processing was again performed using the electric discharge machine by the electrode (that by which what was used previously amended the geometry -- or the electrode of eye small ** is somewhat sufficient) shown in drawing This processing condition is before and after discharge voltage =100V Ip=3A, taup=64microsecond, and taur=256microsecond. The cavity covered with a high configuration precision as a work front face was shown in drawing 15 was obtained. According to this processing, the die-casting die which performs elevated-temperature teeming can be made.

[0040] Here, when performing pulse electric discharge finishing somewhat using the electrode of eye small **, it carries out like the rocking process (eccentric movement is carried out horizontally, rather than an electrode size, it is the method of only an eccentric size processing it greatly, and, thereby, the machined surface granularity of the side and a base carries out the works of the electrode) which an electron discharge method is sufficient as, is known, and is.

[0041] This method of this example carries out the electron discharge method of the configuration of a cavity with difficult processing, makes the inside deposit material, such as fine ceramics, by thermal spraying etc., and makes a it top remelt by the pulse electron discharge method by the usual processing method. It is impossible or difficult to carry out melting with other laser, high-frequency heating, etc., and is the very big advantage of this invention.

[0042] In addition, in the abovementioned example, although the electric discharge deposit and the spraying process were used as a covering means of covering material, it is not necessary to say that other meanses, such as an electrodeposition process and a low-temperature-evaporation method, can be used, and it can use combining various covering meanses.

[0043]

[Effect of the Invention] As explained in full detail above, according to this invention, there are no faults, such as a dimensional change of a base material, a degree-of-hardness (intensity) fall, and coat ablation, and the precise and firm enveloping layer which moreover has the surface characteristics of a request of **, such as corrosion resistance and thermal resistance, by sufficient thickness can be formed easily. for example, the elevated-temperature gas or the steamy bombardment section of a high-temperature-service turbine blade, the die cavity portion which casts elevated-temperature molten-metal hot water, and liquid metal forging-- the shot-blasting nozzle portion of metal mold, other portions (for example, injection-molding-machine pipe portion etc.), and steel-- it can use for coating only a part for the cutting edge of metal mold with fine ceramics etc.

[0044] Moreover, the functionally gradient material to which composition had the so-called inclination functional film which changes gradually to the front face on the base material can also be manufactured cheaply.

[Translation done.]